

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

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| In re application of | Appeal No. |
| Harald KRAUS et al. | Conf. 2464 |
| Application No. 10/588,766 | Group 1792 |
| Filed August 8, 2006 | Examiner Roberts Culbert |
| METHOD FOR SELECTIVE ETCHING | |

APPEAL BRIEF

MAY IT PLEASE YOUR HONORS:

(i) Real Party in Interest

The real party in interest in this appeal is the assignee, LAM Research AG, Villach, Austria.

(ii) Related Appeals and Interferences

Neither the appellant, appellant's legal representative nor the assignee know of any other prior or pending appeals, interferences or judicial proceedings which may be related to, directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

(iii) Status of Claims

Claims 3-5, 8, 11-15 and 17 are pending, from whose final rejection this appeal is taken.

Claims 1, 2, 6, 7, 9, 10 and 16 were cancelled.

(iv) Status of Amendments

There are no outstanding amendments. The claims have not been amended since the April 21, 2009 amendment. These claims were finally rejected by the Official Action mailed August 18, 2009 (the "Official Action"). The claims are as set forth in the Claims Appendix.

(v) Summary of the Claimed Subject Matter

Claim 17, which is the sole independent claim, is directed to a method of selective etching comprising:

(See, e.g., original specification page 2, paragraph [0010].)

providing a first material on a substrate, wherein said first material is HfO₂ or ZrO₂, and said first material is pretreated with an energetic particle bombardment;

(See, e.g., page 2, paragraph [0010], line 3 in light of page 4, paragraph [0029], line 2, paragraph [0031], and paragraph [0032].)

providing a second material on the substrate; and

(See, e.g., page 2, paragraph [0010], line 4.)

selectively etching said first material with a selectivity of at least 2:1 towards said second material by dispensing a liquid etchant onto the substrate surface and generating a flow having a mean velocity v parallel to the surface of the substrate of at least 0.1 m/s,

(See, e.g., page 2, paragraph [0010], lines 7-8.)

wherein said liquid etchant is dispensed in a continuous flow as a free beam or as a liquid stream onto the substrate and spreads over the surface of the substrate.

(See, e.g., page 3, paragraph [0014].)

(vi) Ground of Rejection to be Reviewed on Appeal

The ground of rejection on appeal is whether claims 3-5, 8, 11-15 and 17 were properly rejected as being unpatentable under 35 U.S.C. §103(a) over CHRISTENSON (US 2003/0235985) in view of TANAKA (US 5,032,217) and further in view of BUCHANAN (US 2003/0230549).

(vii) Arguments

None of claims 3-5, 8, 11-15 and 17 are unpatentable over CHRISTENSON in view of TANAKA and further in view of BUCHANAN.

The Examiner offered CHRISTENSON for teaching an etching method. TANAKA was offered for teaching free beam etchant dispersion, and BUCHANAN was offered for teaching pre-treatment

of a material prior to etching, such as by energetic particle bombardment.

The rejection is based on at least two erroneous interpretations of CHRISTENSON: (1) CHRISTENSON suggests an etchant flow velocity parallel to the substrate surface that could be optimized, and (2) CHRISTENSON teaches using HfO_2 and ZrO_2 .

1. CHRISTENSON does not suggest an etchant flow velocity parallel to the substrate surface that could be optimized.

The Examiner acknowledged that CHRISTENSON fails to disclose or suggest the velocity in claim 17.

TANAKA was offered for teaching the optimization of the process variables to arrive at the claimed velocity. For example, the Examiner pointed to TANAKA teaching a 4mm diameter provides a velocity of 0.1 m/s using a volume flow of 0.1 lpm.

However, claim 17 also requires "dispensing a liquid etchant onto the substrate surface and generating a flow having a mean velocity v parallel to the surface of the substrate", and this etchant is dispensed "in a continuous flow as a free beam or as a liquid stream onto the substrate and spreads over the surface of the substrate".

There would have been no reason for one to even approach the claimed continuous flow and flow velocity parallel to the substrate surface based on the teachings of CHRISTENSON for at least two reasons:

a. Etchant flow is not a result effective-variable.

CHRISTENSON is directed to an etching process where the etching results are independent of the equipment and the etchant flow (paragraph [0042] and [0043]):

"The etching process(es) and solution(s) can be used in any equipment where the etching solution is able to contact and etch the high k-material. For instance, the wafers with the high-k material can be immersed in a bath of the etching solution, either static, cascading or otherwise flowing, as in a wet bench." (Emphasis added.)

"The similarity between the etch results noted below in the examples utilizing a small , static volume of etching solution and a centrifugal spray processor with high cross-wafer flow rates indicates that the flow rate of etching solution over the wafer is not critical." (Emphasis added.)

Indeed, Table 5 shows similar results for an immersion (no flow velocity) technique and a spraying technique (a volumetric flow of unknown velocity):

TABLE 5

| Etch rates in A/min of various films immersed in etchant and in a spray processor. | | | | |
|--|---------------|------------------------|------------------------|------|
| | $Zr_xSi_yO_x$ | $Hf_xSi_yO_x$ (60%) | $Hf_xSi_yO_x$ (80%) | TEOS |
| 0.049 wt % HF - Immersion | >29.6 | 25 | 14.8 | 5.0 |
| 0.04 wt % HF - Spray | 80 | 68.0 | 14.8 | 9.9 |
| 0.0049 wt % HF - Immersion | >8.1 | 1.4 | 0.2 | 0.09 |
| 0.0049 wt % HF- Spray | 12.7 | 1.9 | 0.3 | 0.1 |

Thus, CHRISTENSON clearly teaches that the etching process is not affected by either the equipment selected (e.g., for an immersion or spraying technique) or the etchant flow.

It is well established that only result-effective variables can be optimized. Moreover, a particular parameter must first be recognized as a result-effective variable (i.e., a variable which achieves a recognized result), before the determination of the optimum or workable ranges of said variable might be characterized as routine experimentation. *In re Antonie*, 559 F.2d 618, 195 USPQ 6 (CCPA 1977); *In re Boesch*, 617 F.2d 272, 205 USPQ 215 (CCPA 1980); and MPEP § 2144.05 II, B.

For the reasons discussed above, it is clear that CHRISTENSON did not recognize that etchant flow (in terms of volumetric flow or surface velocity) as a result-effective variable. Indeed, had CHRISTENSON realized the effect of a flow velocity parallel to the surface, CHRISTENSON certainly would not have suggested immersion in a bath of a static solution (e.g., as disclosed in paragraph [0043].)

This is in contrast to the claimed invention, where the cross-wafer flow rate of the etchant is deemed critical.

**b. Etchant flow is not continuous
and parallel to the surface.**

As CHRISTENSON uses an immersion or spray technique to dispense the liquid etchant, there is no etchant flow having a mean velocity v parallel to the surface of the substrate.

That is, the immersion technique in CHRISTENSON corresponds to submerging the wafer into the liquid etchant, and the spray technique results in droplets. Neither technique, however, results in "dispensing in a continuous flow as a free beam or as a liquid stream onto the substrate and spreads over the surface of the substrate", wherein "flow having a mean velocity v parallel to the surface of the substrate" as claimed.

Thus, there was no continuous flow onto the substrate with a velocity parallel to the substrate surface to optimize.

**2. CHRISTENSON teaches away
from using either HfO_2 or ZrO_2 .**

The objective of CHRISTENSON is to etch high-k films in an effective, controllable and repeatable manner. CHRISTENSON accomplishes this objective using an etching composition that "is an aqueous solution that comprises an unconventionally dilute concentration of one or more fluoride species." (par.[0013])

In paragraph [0022], CHRISTENSON discloses:

"It has been discovered that dielectric materials comprising at least two elemental constituents in addition to any oxygen may be favorable etched using the dilute fluoride containing etching solution of the present invention. While not wishing to be bound by theory, it is believed that the favorable etch characteristics are related to the crystalline structure of the high-k dielectric films. Conventionally, a unary high-k dielectric material, i.e., a material comprising only one elemental constituent other an oxygen (e.g., HfO_2 or ZrO_2), are highly resistant to dilute etchants."

However, it is believed that incorporating at least two elemental constituents in addition to optional oxygen disrupts the crystalline lattice to a sufficient degree such that the material is more susceptible to etching." (Emphasis added.)

That is, for the purpose of using "an aqueous solution that comprises an unconventionally dilute concentration of one or more fluoride species" etching materials with HfO_2 or ZrO_2 are not desired by CHRISTENSON.

Instead, the preferred materials of CHRISTENSON are generally described as:

[0024] A wide variety of dielectric materials may be used as high-k dielectric materials of the invention. In some embodiments, preferred high k dielectric materials comprise at least two constituents selected from Zr, Hf, Si, Ge, Y, As, N, and Al. In such embodiments, the material may further comprise additional non-metal constituents such as B, P, combinations of these, and the like. In some embodiments, if the material comprises both Si and N, it is further preferred that such embodiments further comprise at least one additional constituent such as Zr, Hf, Ge, Y, As, B, P, combinations of these, or the like.

The specific materials include (par. [0025] and [0026]):

$\text{M}_z\text{Si}_y\text{O}_x$, wherein M is one or more metals, y has a value such that the silicate comprises 10% to 90%, preferably 10% to 50% mole fraction Si compared to the other metal(s), and x and z are selected to satisfy stoichiometry. Such silicates optionally may also include one or more additional constituents, as desired, of which B, P, Y, As, Ge, N, Al, combinations of these, and the like are representative.

[0026] Specific examples of silicates include, e.g., HfSiO_4 ($k=12$), ZrSiO_4 ($k=13$), $\text{Hf}_{0.6}\text{Si}_{0.4}\text{O}_2$ (k of about 14, commonly referred to as HfSiO (40%)), combinations of these, and the like. Other examples of combinations of elemental oxides include $\text{Zr}_z\text{Hf}_y\text{O}_x$, $\text{Hf}_z\text{Al}_y\text{O}_x$, and $\text{Zr}_z\text{Al}_y\text{O}_x$, where the ratio of $z:y$ preferably is in the range of 1000:1 to 1:1000 and x satisfies stoichiometry. Some other materials under consideration as silicates or in combination with other metals are listed by "A Thermodynamic Approach to Selecting Alternative Gate Dielectrics," by D. G. Schlom, MRS Bulletin, 27 (3), 198-204, (2002).

In light of the above excerpts, one would have expected that by selecting a first material on a substrate, "wherein said first material is HfO_2 or ZrO_2 " (according to independent claim 17), the substrate would have been resistant to the etching compositions utilized by CHRISTENSON. That is, one would have expected HfO_2 or ZrO_2 to have rendered the dielectric materials unsatisfactory for the etching process of CHRISTENSON directed to a particular etching composition.

If proposed modification would render the prior art invention being modified unsatisfactory for its intended purpose, then there is no suggestion or motivation to make the proposed modification. *In re Gordon*, 733 F.2d 900, 221 USPQ 1125 (Fed. Cir. 1984) and MPEP 2143.01 V.

Therefore, one of ordinary skill in the art would have been strongly discouraged from selecting "a first material on a substrate, wherein said first material is HfO_2 or ZrO_2 " as presently claimed, for the intended purpose of CHRISTENSON.

3. Conclusion

As CHRISTENSON fails to teach or suggest these features for which it was offered, neither TANAKA nor BUCHANAN can remedy these shortcomings for reference purposes.

Indeed, BUCHANAN, which is the closest prior art, teaches HfO_2 , ion-bombardment, and selective wet etching, but BUCHANAN fails to disclose or suggest a functional effect of the

flow velocity on the selectivity. Also, for the reasons discussed above, one of ordinary skill in the art would have been discouraged from including HfO_2 , as taught by BUCHANAN, in the material of CHRISTENSON, as it would have rendered the material unsatisfactory for etching with the dilute solutions required by CHRISTENSON.

Therefore, a *prima facie* case of obviousness has not been made for the rejection of independent claim 17 and dependent claims 3-5, 8, 11-15.

From the foregoing discussion, it is believed to be apparent that the rejection of claims claim 17 and dependent claims 3-5, 8, 11-15 is improper and should be reversed. Such action is accordingly respectfully requested.

Respectfully submitted,

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(viii) **Claims Appendix**

3. The method of claim 17, wherein the point of impact of said liquid etchant stream is moved across the surface of the substrate in a time sequence.

4. The method of claim 17, wherein said liquid etchant is dispensed at a volume flow of at least 0.05 l/min.

5. The method of claim 17, wherein said substrate is rotated while exposed to said liquid etchant.

8. The method of claim 17, wherein the second material is silicon dioxide and the liquid etchant comprises fluoride ions.

11. The method of claim 17, wherein said liquid etchant is selected from the group consisting of:

a solution comprising fluoride ions and an additive for lowering dielectric constant of said solution,

an acidic aqueous solution comprising fluoride ions;
and

an acidic aqueous solution comprising fluoride ions and an additive for lowering dielectric number.

12. The method of claim 11, wherein said liquid etchant comprises an analytical concentration of less than 0.01 mol/l of fluoride ions, wherein said analytical concentration is calculated as F^- .

13. The method of claim 17, wherein said liquid etchant comprises fluoride ions and has a pH less than 3.

14. The method of claim 2, wherein the liquid etchant is dispensed at a volume flow of at least 0.5 l/min.

15. The method of claim 11, wherein the additive for lowering dielectric number, in the acidic aqueous solution comprising fluoride ions, is an alcohol.

17. A method of selective etching comprising:
providing a first material on a substrate, wherein said first material is HfO_2 or ZrO_2 , and said first material is pretreated with an energetic particle bombardment;

providing a second material on the substrate; and

selectively etching said first material with a selectivity of at least 2:1 towards said second material by dispensing a liquid etchant onto the substrate surface and generating a flow having a mean velocity v parallel to the surface of the substrate of at least 0.1 m/s,

wherein said liquid etchant is dispensed in a continuous flow as a free beam or as a liquid stream onto the substrate and spreads over the surface of the substrate.

(ix) **Evidence Appendix**

None.

(x) Related Proceedings Appendix

None.